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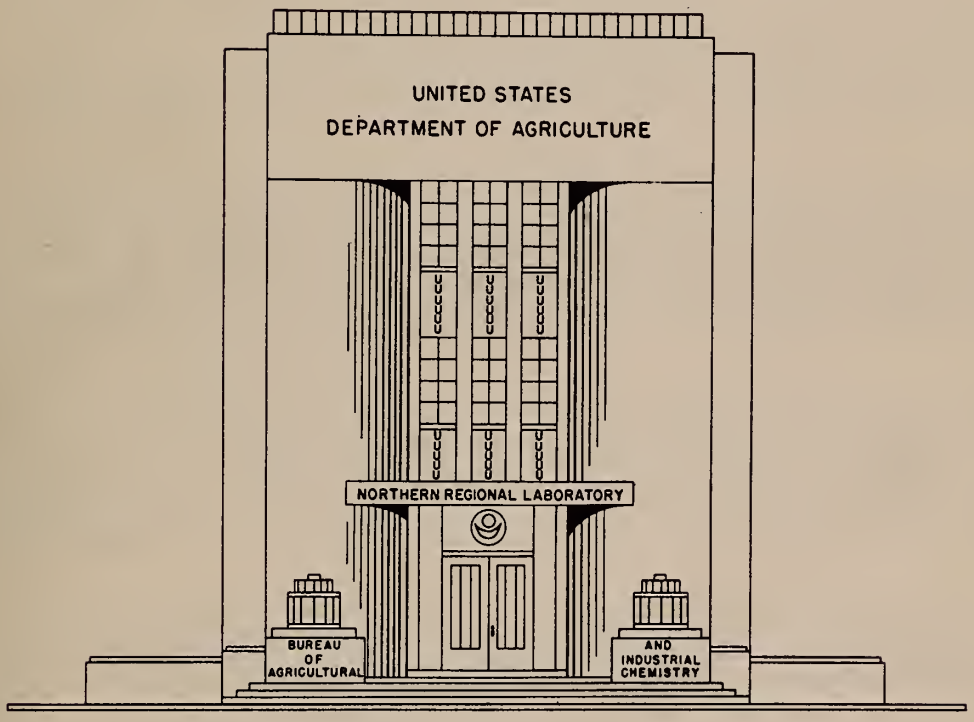
MANUFACTURE OF CELLULOSE PULPS FROM STRAW



By S. I. Aronovsky

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PEORIA, ILLINOIS

JULY 1950

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MANUFACTURE OF CELLULOSE PULPS FROM STRAW

By

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Straw pulp is an important ingredient of paper and board in all countries where straw is grown and where paper and board are produced. Bleached straw pulp is blended with wood and rag pulps for many grades of fine paper and board, particularly in Europe and South America. In North America only the coarse type of straw pulp, with one exception, is currently produced, mainly for making corrugating paper although small amounts are also used for straw chip, shirt board, egg case fillers, and similar products. The exception is a small amount of unbleached or semi-bleached chemical wheat straw pulp for brown cigarette paper for the Central and South American trade. White cigarette paper is made in America almost entirely from seed flax tow which constitutes about 20-25 percent by weight of seed flax straw.

History.--Cereal grain straws are among the oldest of papermaking materials. Use of straw for paper, along with bamboo and rags, dates back to the early Chinese era of papermaking. The straws and other papermaking materials were generally defibered by softening in water and then macerated by hand or, later, by stamping machines. The pulps so produced were diluted and made into sheets of paper on hand molds. The wet sheets were allowed to dry in the air and sun.

The first chemical straw pulp was produced in 1800 by Mathias Koops from Mainz, Germany, and the first commercially successful straw pulp process took place at Chambersburg, Pennsylvania, in 1831 producing binder board on a cylinder machine at the rate of 100 pounds per hour. Bleached straw paper was first produced by John B. Davis at Rensselaer, New York.

In the early days of its manufacture, straw paper was widely used for wrapping meats and was not replaced as butcher paper until the early part of this century. Newsprint was produced from straw pulp mixed with rag and other available waste fibrous materials. The stronger types of papers were made from a mixture of straw pulps with those made from rags, rope, or bagging.

Straw, rags, and other available waste fibrous products continued as the raw materials for paper until about 1860 when commercial production of wood pulp began. The rapid expansion of wood pulp production supplanted the use of straw, particularly in the United States, for practically all types of paper except corrugating paper. Some European

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[1] Prepared at the invitation of the VIII International Congress of Agricultural Industries by Dr. S. I. Aronovsky, In Charge, Pulp and Paper Section, Agricultural Residues Division, Northern Regional Research Laboratory, Peoria, Illinois, U. S. A., one of the laboratories of the Bureau of Agricultural and Industrial Chemistry; read before this Congress July 9-15, 1950 at Brussels, Belgium by Dr. G. E. Hilbert, Chief, Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture, Washington, D. C.

countries, however, notably Holland, Germany, France, and Italy, have continued to produce and use straw pulp for fine papers and boards as well as for the coarser grades. Argentina, Italy, Holland, and other countries which must import pulpwood or wood pulp at relatively high cost, produce and use straw pulps as major ingredients of practically all of their papers and paper products.

The rapid expansion of wood pulp production since the early part of the present century, together with the tremendous expenditure of lumber and pulpwoods in the two world wars during this period have focused world attention sharply upon the relatively low reserves of coniferous pulpwoods, the major raw material for the paper and board industries. Many wood pulp mills in North America are finding that transportation represents an ever increasing portion of manufacturing costs, as the coniferous pulpwood supplies recede farther and farther from the mill sites. This fact together with the increased cost of woods labor has caused the paper industry to use the faster growing hardwoods and to consider seriously the stems of annual crops as supplementary raw materials.

Contrary to the situation with pulpwood, straw and other fibrous agricultural residues are renewed annually wherever grain and other food and feed crops are grown. Cereal grain straws are preferred to the other crop residues for pulp and paper because of their relatively low content of pith and other structural parts generally found unsuitable for papermaking. It must be emphasized that only that portion of cereal grain straws or other agricultural residues *surplus* to farm needs can be considered for industrial utilization. Where good agricultural practice requires these materials for litter and bedding or for the soil, these uses should be considered foremost.

Availability of straw.--Cereal grains constitute a major staple of human nutrition. Straw, a co-product of grain production, is available wherever grain is grown. The estimated amounts of small grain straw produced in 1947 on the various continents are given in table 1. Somewhat larger amounts were produced in 1948 and 1949.

The enormous annual world production of nearly a billion tons of small grain straw staggers the imagination. It is estimated that only about 49 percent of the straw grown is generally recoverable for farm and non-farm use. This percentage varies with requirements and cultural practices of the different lands. The remaining 51 percent of the total straw produced, including stubble, short straw, and chaff, is left on the ground or plowed under to supply humus and plant food. In the more densely populated, intensively cultivated, arable areas of the world, particularly the Orient and some parts of Europe, a large proportion of the recoverable straw is used for fuel. A considerable amount of straw in these areas is also returned to the soil, mostly as manure. In North America, however, where practically all small cereal grains are combine harvested, it is estimated that almost half the recoverable straw, or about 40 million tons, is either burned or left to rot on top of the ground; neither practice yields much of value to the soil or the farmer. Similar situations probably exist in other lands with large farming areas not too densely populated.

Suitable types of straw.--Commercial and laboratory experience in Europe and the Americas shows that wheat and rye straws are preferred over other straws and produce stiffer corrugating paper and stronger fine papers. The leafy character of oats, rice, and barley straws probably accounts for the relatively low yields and strength values of their pulps, but this feature makes them valuable as a supplementary feed for livestock, thus providing a good farm use and a competitive market.

TABLE 1.--Estimated world production and industrial availability of small grain straw in 1947

Continent	Straw production and availability						
	Wheat[2]	Rye[3]	Oats[4]	Barley[5]	Rice[6]	Flax[7]	Total
	In 1000 tons						
North America							
Production	120,540	3,429	38,896	15,045	3,436	4,452	185,798
Available[1]	59,065	1,680	19,059	7,372	1,684	2,181	91,041
Europe							
Production	71,050	43,313	31,876	19,824	1,844	412	168,319
Available[1]	34,815	21,223	15,619	9,714	904	202	82,477
Asia							
Production	105,700	1,374	2,314	24,249	224,476	1,285	359,398
Available[1]	51,793	673	1,134	11,882	109,993	630	176,105
U.S.S.R.							
(Europe and Asia)							
Production	61,250	80,500	21,320	10,974	—	1,279	175,323
Available[1]	30,013	39,445	10,447	5,377	—	627	85,909
South America							
Production	21,350	1,225	1,274	1,876	5,235	3,108	34,068
Available[1]	10,462	600	624	919	2,565	1,523	16,693
Africa							
Production	9,100	150	572	3,717	5,655	50	19,244
Available[1]	4,459	74	280	1,821	2,771	25	9,430
Oceania							
Production	16,275	—	978	836	162	29	18,280
Available[1]	7,975	—	479	410	79	14	8,957
Total							
Production	405,265	129,991	97,230	76,521	240,808	10,615	960,430
Available[1]	198,582	63,695	47,642	37,495	117,996	5,202	470,612

[1] Calculated as 49 percent of the total straw produced.
[2] Production calculated as 70 tons straw per thousand bushels of wheat.
[3] Production calculated as 87.5 tons straw per thousand bushels of rye.
[4] Production calculated as 26 tons straw per thousand bushels of oats.
[5] Production calculated as 35.4 tons straw per thousand bushels of barley.
[6] Production calculated as 33.8 tons straw per thousand bushels of rice.
[7] Production calculated as 84 tons straw per thousand bushels of flax.

Collection and transportation.--Most cereal grains in North America are now harvested, from Texas in the South to Canada in the North, in a season that lasts about 2 months. The change in harvesting methods brought about a serious apparent straw shortage at the same time that larger amounts of straw were actually being produced. This was because of a lack of sufficient and suitable economical equipment for picking up the straw left scattered on the fields by the combine. In recent years, however, such apparent shortage has been largely overcome by availability of low-cost, one-man pick-up balers. The straw-consuming paper mills in the United States who had to go hundreds of miles from their plants to obtain sufficient straw, now obtain their supplies within 25 to 50 miles from the mill.

The shortened harvest season involves storage of a major portion of the baled straw and, consequently, the exposure of more straw to weather and microbial attack. This problem has been largely solved in the last few years, through cooperative work between the strawboard industry and the Northern Regional Research Laboratory. The tops of the piles or ricks of straw bales are now dusted with a relatively small amount of borax, which is an excellent, economical preventative of microbial degradation of straw exposed to rain or snow. Other methods of straw preservation being tried include sisal kraft paper, sheet metal, and loose straw as coverings.

Physical structure.--Culms of small grain straw are erect, elastic, generally tubular structures, separated at intervals by nodes--vascular bundles crowded and interlaced to form a strong diaphragm between the internodes. Straws grow about 2 to 6 feet tall depending on variety and cultural conditions. They usually have six internodes which increase in length from base to apex of the straw. The wall thickness of the straw decreases with the distance from the ground.

The bast cells or fibers from the internodes form the major part of straw pulp. They are comparatively short and slender with sharp pointed ends. Dimensions of these straw fibers vary somewhat with the kind of straw, but dimensional differences between straw fibers and the common wood fibers are generally greater than those among the various straw fibers themselves, as shown in table 2. The straw fibers are somewhat longer than those from esparto, shorter than those from coniferous woods, and approximately as long as the fibers from deciduous woods. The excellent paper-formation characteristics of straw fibers are indicated by their relatively high ratio of average length to diameter.

TABLE 2.--Dimensions of fibers from various plants and woods

Source of fiber	Average length	Average diameter	Ratio av. length/diameter
	Microns	*Microns*	
Wheat, barley, oats, rye straws	1,480	13.3	111:1
Rice straw	1,450	8.5	170:1
Esparto grass	1,100	9.2	120:1
Sugarcane bagasse	1,700	20.0	85:1
Red spruce wood	2,700	32	85:1
Red gum wood	1,600	32	50:1

Straw pulp also contains epidermal cells, platelets, serrated cells, and spirals, all being small and relatively nonfibrous. They come mainly from the vestige of pith on the inner part of the stem, from the nodes and rachises (heads), from the leaf blades and sheaths, and from the chaff (a small amount of which nearly always accompanies the straw).

Chemical composition of straws.--Proximate chemical analyses of several American straws are shown in table 3. The range in values of the individual straw constituents reflects the effect of both straw variety and of soil and cultural conditions of growth. This range in values is similar to that generally found for woods and other fibrous plant materials.

TABLE 3.--Proximate composition of some American straws

Item	Straw					
	Wheat	Rye	Oats	Barley	Rice	Seed flax
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Ash	6-8	4-6	6-8	7	16-19	5
Solubility in alcohol-benzene	2-5	3-5	2-4	5	4-5	4
Solubility in water	10-18	10-14	9-14	16	13-15	14
Lignin	17-19	18-19	18-20	15	12-14	23
Pentosans	27-32	28-31	27-30	25	23-25	25
Cross & Bevan cellulose	50-54	50-54	45-53	48	46-49	47
Alpha-cellulose	33-38	33-38	31-39	34	28-36	34

All the straws, excepting seed-flax straw, contain less lignin than is found in pulpwood. Straws also have lower cellulose and higher pentosan contents. The higher cellulose and pentosan contents of wheat and rye straws, compared to other straws, account for the preferred position of the wheat and rye straws for pulp and paper. Rice straw is easily characterized by its high ash content, mainly silica (SiO_2).

Technology of straw pulping.--Modern technology of pulp and paper manufacture has been centered almost entirely on wood as the raw material. While a voluminous literature has accumulated on the production of pulp and paper from straw and other agricultural residues, a survey of the literature leads to the conclusion that the previous approach to this problem, namely, the production of cheap substitutes from farm residues, was unsound both technologically and economically. Most reported work deals with scattered experiments in educational institutions and mill laboratories, and with commercial trial runs wedged into production schedules. The laboratory work, with a few exceptions, was carried out without regard to the technology and economics of commercial operation. The exceptions refer to some excellent work reported about 20 years ago in the United States and to recent studies by Jayme in Germany and by Ritman and his coworkers in the Netherlands. In the large-scale mill trials the inconclusive results of

one or several runs, made without suitable control because of production schedule requirements, were frequently used to determine the success or failure of the process or modification involved. Thus a new method of attack appeared necessary for successful solution of the problem of economic production of pulp from straw and other agricultural residues.

Straw pulping at the Northern Laboratory.--After considerable thought it was decided that the soundest approach would be to determine the properties and characteristics of the various agricultural residues and the fundamental differences among themselves and between them and other papermaking materials. Then, by capitalizing on the particular properties of the residues it should be possible to establish their rightful place in industry on a utilitarian and economic basis. Several examples of commercial enterprises in the pulp and paper field, wherein success resulted from recognition and utilization of the specific properties of the agricultural residue materials involved, are: excellent lightweight book and Bible paper from esparto, stiff corrugating paper from cereal straws, superior insulating board from sugarcane bagasse, and cigarette paper from seed flax tow. These examples indicate the soundness of the stated plan of attack, which was also approved by a large number of mill operators and technical men.

The first work in this program arose with the war emergency. It was found that the very thin barley and rice straw alpha-pulp fibers were suitable for replacing the fine asbestos fibers used with coniferous alpha-cellulose pulps to produce the filters for gas masks. The blend of fine straw fibers with the coarser wood fibers produced a filter with a high retention of smoke and fume particles without decreasing the permeability of the filter pad to air.

Coarse straw pulp.--Attention was also turned to the problems of the strawboard industry in the United States, which consumes about 500,000 to 600,000 tons of straw annually. Many strawboard mills have excellent laboratories and equipment designed for testing the finished paper and for developing new conversion products. They had done relatively little work, however, to improve the pulping of straw. A survey was made of the pulping conditions used in the various mills and studies were begun at the Northern Laboratory aimed at improving the quality of strawboard pulp. Cooperative efforts by the strawboard mills and the Northern Laboratory have produced excellent results. It was found that caustic soda, sodium sulfite, or mixtures of these chemicals in small proportions produced pulps with considerably greater crush resistance than had been obtained heretofore by using lime either alone or as the major pulping chemical. The slightly lower yields of pulp resulting from the use of the soda alkalies are more than offset by the better strength and operating characteristics of the pulps produced. Most strawboard mills in America have now gone over to the use of these improved cooking formulas.

At the same time, cooperative work with the strawboard mills, farm equipment manufacturers, producers of chemical preservatives, and the Technical Association of the Pulp and Paper Industry was initiated to improve the economics of harvesting, baling, storing, and preserving the straw. As a result, combine-harvested straw is now collected and baled with one-man, automatic wire-tie balers, and delivered to the mills in bales having a density of 10 pounds or more per cubic foot. Combined straw contains considerably less chaff than the binder-harvested material. Treatment with borax, as mentioned earlier, appears to be a practical solution of the preservation of uncovered straw in storage.

Fine straw pulp.--A much broader field for straw lies in the production of pulps for fine and bleached specialty papers and boards. Such bleached products are in commercial production and use in Europe, South America, and the Orient, but not yet in North America.

One serious drawback to straw for fine pulps and papers has been the reported low yields of pulp produced, based on its relatively low alpha-cellulose content, as compared with that from pulpwoods. When the total carbohydrate portion, the holocellulose, of straw is considered, however, it is found to be approximately equal to that obtained from most pulpwoods. Many experiments were conducted at the Northern Laboratory in attempts to develop an economic process for producing a holocellulose pulp from straw. All of the existing, well-known commercial pulping processes were also investigated with wheat straw as the raw material. As a result, it was determined that the neutral sulfite process came nearest to producing a holocellulose type of pulp, yielding approximately 50 percent of a strong, bleached pulp, based on original straw. This pulp has strength characteristics at least equal to those of softwood sulfite pulp, except for tear resistance, a property which is almost directly correlated with average fiber length of the pulp. Many mills in Europe, particularly in Italy, are now using this process successfully.

Mechano-chemical pulping.--About a year after the neutral sulfite process for straw was established, the Northern Laboratory announced the mechano-chemical process--a new and revolutionary method for producing pulps from straw in high yields with excellent strength characteristics. Using the same amounts of chemicals, based on straw, mechano-chemical pulping for coarse strawboard pulp requires cooking for only 1 hour at 96° to 100° C., as compared with 5 hours at 140° C. (40 p.s.i.) in pressure cooking. The yields and properties of the pulps prepared by these two methods are quite similar. Runs of 24- and 48-hour duration in commercial Hydrapulpers have corroborated fully the results obtained with the 3-foot laboratory unit. In fact, the commercial operation was considerably better than expected from the laboratory results. One strawboard mill in the United States is seriously considering changing over to the mechano-chemical process.

In cooking straw for fine pulp, the mechano-chemical process requires only about 1/2 hour at 96° to 100° C. for producing an excellent kraft or soda pulp, in contrast to the 2 hours at 170° C. (100 p.s.i.), using the same amount of chemicals based on straw. The yields of the mechano-chemical kraft and soda straw pulps exceed by 6 to 8 percent those obtained from cooking under pressure. The alkaline pulps obtained by either method are considerably stronger than neutral sulfite straw pulps and approach softwood kraft pulp in all strength characteristics except tear resistance. This new process is not applicable to wood chips or to fibrous materials having a dense woody structure. Preliminary tests have shown it to be applicable, however, to other members of the grass family such as sugarcane bagasse or cornstalks. The nodes, rachises, and seed kernels are swollen and softened but not pulped, and they are readily removed from the pulp by riffling and screening.

The mechano-chemical process produces a pulp with a higher hemicellulose or pentosan content than was present in the original straw, or in pulp produced by any other pulping method; straws containing 26 to 28 percent pentosans give pulps with about 33 percent pentosans. Very little loss of the original alpha-cellulose occurs with this pulping process. Furthermore, the ash content of the mechano-chemical pulp is considerably below that of the same type of pulp produced by cooking under pressure. These facts all indicate that the mechano-chemical process approaches the ideal in pulping, that is, delignification with a minimum of attack on the carbohydrate constituents of the raw material.

General considerations.--History proves that the progress of civilization in any part of the earth is directly correlated with the average standard of living in that particular location. It also shows that the standard of living has been increasing since ancient times, with occasional setbacks due to such natural catastrophes as floods, earthquakes, and disease, and to man-made catastrophes, wars.

Better means of communication is one of the signs of advancing civilization and improved standard of living, whether it be the cause or the result of such advance. Better communication means better education and brings people closer together. The written word or sign is probably the most important means of communication, and has been since the stone tablets in ancient times. Today, paper constitutes the essential material for education and communication.

Thus, the degree to which paper or paper products is used by a nation or continent gives a fair indication of its standard of living. The United States, with probably the highest standard of living in the world today, has an annual per capita consumption of about 350 pounds of paper and board products. The estimated per capita consumptions of other areas, in order of decreasing use of these materials are: Canada 256 pounds, Northern Europe 116 pounds, Oceania 99 pounds, Continental Europe 49 pounds, Latin America 17 pounds, Africa 6 pounds, Near East 2.6 pounds, and Asia 2.4 pounds. The known low average standard of living in Asia and the Near East is confirmed by these figures.

Most of the world's pulp is produced at present from coniferous woods, which grow mainly in the North Temperate Zone. Outside of the virgin forests of Alaska and parts of Russia including Siberia, the coniferous wood stands of the world have already been reduced to a considerable extent. The present rate of cutting of these wood stands is at least equal to, if not in excess of, annual replacement growth. Now, if the world consumption of pulp and paper products were increased by 1 pound per capita, an additional 1 million tons of pulp and paper products or approximately 2 million tons of raw material would be required. An increase in 10 pounds per capita for the world population of 2 billion would require an additional 20 million tons of fibrous raw material per year. Such an increase, which might reasonably come about in the next few years, would sorely tax the pulpwood resources of the world if the increased production came about through the use of wood.

The amounts of available straw, annually surplus to the needs of the farms, on the other hand, are more than sufficient to take care of such additional pulp and paper requirements. It seems incompatible with good economy to allow these annual fibrous raw materials to go to waste while, at the same time, the natural forest resources are being depleted. No one would think of throwing away the annual interest accruing from an investment while at the same time drawing on the investment principal for current expenses. Yet, that is exactly what is being done when wood is cut and pulped to do a job which can be done as well or better by straw or other annual fibrous residue available in excess. Again, this does not mean that straw fiber should be used indiscriminately for all papers and paper products. The various fibers should be blended so that each fiber will contribute its optimum characteristics to give a final paper or product with the desired properties.

Conclusions.--It is evident from the foregoing that sufficient straw and other agricultural residues are annually available in the world to meet the expected increase in paper and board requirements for many years to come. Intelligent use of the various types of fibrous residues available can accomplish this increase in paper production without excessive drain on the pulpwood and timber resources. The expected improvements in technology from continued and increasing use of straw and other agricultural residues, should greatly advance the overall economy of the world pulp and paper industry.

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